650

responding hydroxamic acids, fractionating these, and reconverting the pure oleohydroxamic acid to oleic acid.

The present procedure [9] is a simplification of the methods of Brown and Shinowara [5] and of Wheeler and Riemenschneider.[6] It gives higher yields of a somewhat lower-quality product.

The procedure described is more satisfactory than those requiring the crystallization of soaps of oleic acid. For a review of these methods see ref. 5.

METHYL RICINOLEATE

$$CH_3(CH_2)_5\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2CH=CH-(CH_2)_7CO_2CH_3$$

Mol. wt. 312.5 ($C_{19}H_{36}O_3$)

Submitted by DANIEL SWERN and E. F. JORDAN, JR., Eastern Regional Research Laboratory, Philadelphia.
Checked by L. H. MASON and H. E. CARTER, University of Illinois, Urbana.

I. Principle

$$\text{Castor oil} + CH_3OH \xrightarrow{NaOCH_3} CH_3-(CH_2)_5-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH=CH-(CH_2)_7-CO_2CH_3 + \underset{\displaystyle OH}{\underset{|}{CH_2}}-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}$$

II. Procedure

One thousand grams of U.S.P. castor oil are added to a solution of 3 gm. of metallic sodium in 2 l. of anhydrous methanol in a 12-l. Pyrex round-bottomed flask. The reaction mixture is refluxed for 45 minutes and then diluted, with stirring, with about 7 l. of water containing 25 ml. of 6 *N* hydrochloric acid. The lower aqueous layer is siphoned off and discarded. The methyl esters are transferred to a 4-l. separatory funnel and washed with water until free of chloride ion. The crude, washed esters

[9] D. Swern, H. B. Knight, and T. W. Findley, *Oil & Soap*, **21**, 133 (1944).

are dried by heating to 100–105° under moderate vacuum in a stream of inert gas. The yield at this point is 970–980 gm. of a pale yellow oil. This is fractionally distilled *in vacuo*.[1] The fraction distilling at 185–187°/2 mm. consists of essentially pure methyl ricinoleate. The yield is 670–680 gm. (84–85% of the theory based on the assumption that castor oil contains 80% of ricinoleic acid).

III. Properties and Purity of Product

Methyl ricinoleate is a colorless, odorless oil melting at −6°. It gives the following constants: refractive index, $n_D^{20} = 1.463$; specific rotation, $[\alpha]_D^{25} = +5.05°$ (5% solution in acetone); iodine number, 81–82; saponification equivalent, 312–313; hydroxyl, 5.5%.

IV. Methods of Preparation

Methyl ricinoleate was prepared by methanolysis of castor oil followed by fractional distillation and low-temperature solvent crystallization.[2] The present procedure is that of Kass and Radlove.[3]

[1] A column with a low pressure-drop should be used to avoid pot temperatures much in excess of 220°. In addition, the column should have a fairly high throughput to keep the distillation time as short as possible. A Vigreux column, 3 ft. long and 1 in. in diameter (five theoretical plates), electrically heated and well insulated, is satisfactory. The checkers found that a vacuum-jacketed silvered Vigreux column gave lower yields than an electrically heated one.

[2] J. B. Brown and N. D. Green, *J. Am. Chem. Soc.*, **62**, 738 (1940).

[3] J. P. Kass and S. B. Radlove, *J. Am. Chem. Soc.*, **64**, 2253 (1942).